

## [54] METHOD OF CHEMICALLY POLISHING METALLIC OXIDES

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[58] Field of Search ..... 156/17, 20, 2, 6; 252/79.1, 79.5, 79.3, 80, 81, 398; 148/23, 28; 117/114 R, 106 R, 107; 134/26 X

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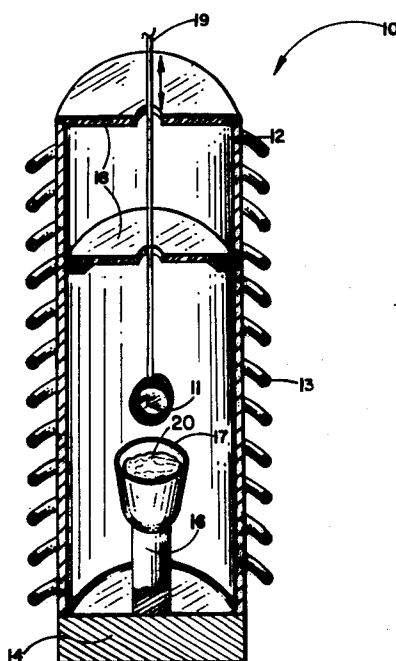
## [57] ABSTRACT

A composition for forming a molten salt used as a

chemical polishing flux and a polishing sequence employing the flux. In an exemplary embodiment, a method of polishing a metallic oxide substrate comprises the steps of forming a molten flux from approximately a 30:1 to 50:1 weight ratio of lead monoxide and boric anhydride at a temperature within the approximate range 1,100°–1,200°C; bringing the flux to thermal equilibrium at a predetermined temperature suitable for establishing a desired rate of dissolution of the substrate material; moving the substrate at a controlled rate toward the molten flux; and immersing the substrate in the molten flux for a sufficient time to strip a predetermined thickness of material from the surfaces of the substrate. The dissolution rate may be varied by changing the temperature of the flux and/or by adding one or more constituents to the flux to vary the saturation point thereof. A controlled rate of withdrawal of the substrate from the flux may be used to form a protective coating on the stripped substrate surfaces. Because the coating can be removed by compatible liquid phase epitaxy systems, liquid phase epitaxy may be used to grow films on the substrate without intermediate cleaning steps.

Alternatively, the flux may be formed by combining boric anhydride ( $B_2O_3$ ) with one or more of lead monoxide ( $PbO$ ), lead fluoride ( $PbF_2$ ), barium oxide ( $BaO$ ), barium fluoride ( $BaF_2$ ), iron oxide ( $Fe_2O_3$ ), vanadium pentoxide ( $V_2O_5$ ) and lithium carbonate ( $Li_2CO_3$ ).

8 Claims, 1 Drawing Figure



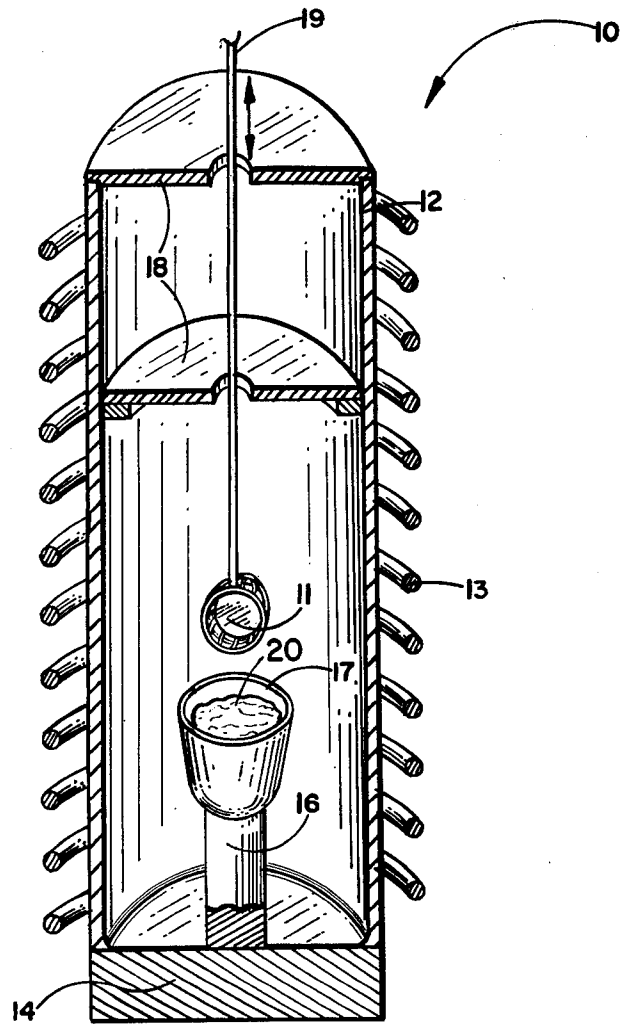


FIG. 1

## METHOD OF CHEMICALLY POLISHING METALLIC OXIDES

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to methods of polishing substrates. More particularly, this invention relates to a chemical polishing flux and to a process utilizing the flux to polish metallic oxide substrates.

#### 2. Description of the Prior Art

The mechanical polishing processes currently used to impart smooth surfaces to insulating substrates frequently create surface defects therein. The defects may be produced by adhering particles of the polishing compound or other extraneous material to the surface of the substrate, by embedding matter in the substrate surface, and by stressing the substrate surface. Such defects deleteriously affect the electronic and magnetic properties of any films that are subsequently grown on the substrate. For example, if a magnetic bubble domain film is grown on the defective substrate, bubble domains generated therein may be pinned at the defect sites.

Generally, where a high degree of surface perfection is required, a multi-step chemical polishing process must be used after the mechanical polish. The known chemical polishing processes typically comprise the steps of stripping the substrate surface in a hot etchant such as ortho-phosphoric acid or mixtures of phosphoric and other acids, quenching the substrate from the hot acid, applying a cleaning agent to remove the acid from the substrate and, frequently, washing and drying the substrate.

As may be appreciated, it is highly desirable to have a polishing procedure that quickly and effectively strips material from the surface of a substrate without requiring the use of a lengthy, post-polish surface preparation procedure.

### SUMMARY OF THE INVENTION

A flux for polishing substrates is formed from various combinations of constituents such as lead monoxide (PbO), boric anhydride ( $B_2O_3$ ), lead fluoride ( $PbF_2$ ), barium fluoride ( $BaF_2$ ), barium oxide (BaO), iron oxide ( $Fe_2O_3$ ), lithium carbonate ( $Li_2CO_3$ ), and vanadium pentoxide ( $V_2O_5$ ). An exemplary chemical polishing flux may be formed from approximately a 50:1 weight ratio of lead monoxide and boric anhydride.

The chemical polishing flux may be used to polish substrate surfaces by forming a molten flux from the constituents of the flux; moving a substrate at a controlled rate toward the molten flux; and immersing the substrate in the molten flux for a time sufficient to remove a predetermined thickness of material from the substrate.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view, partially cut away, of apparatus suitable for practicing the method of the present invention.

### DESCRIPTION OF A PREFERRED EMBODIMENT

The composition of the present invention is used to provide a molten salt that is useful as a chemical polishing flux. Typically, the base constituents of the exemplary composition, lead monoxide (PbO) and boric anhydride ( $B_2O_3$ ), are used in weight rates of between

30:1 to 50:1. However, a weight ratio of approximately 50:1 has given particularly good results. The molten flux formed from these constituents acts as a solvent for garnet and other metallic oxide materials and dissolves or strips the surfaces of substrates formed from such materials at a controllable rate. In stripping a substrate surface, the flux removes surface defects, yet replicates the prior contour and smoothness of the surface. In addition, the flux may be modified by the addition of constituents that are compatible with the basic flux constituents and the substrate material and that alter the dissolution rate provided by the flux.

Referring now to FIG. 1, there is shown a partial, perspective view of a cylindrical furnace system, designated generally by the reference numeral 10, suitable for using the aforementioned salt flux constituents to chemically polish a substrate 11. The furnace system 10 comprises a cylindrical insulative wall 12 and a heat source such as a coil 13. A vestibule block 14 supports the wall 12 and a pedestal 16. A crucible 17 is positioned on the pedestal 16 for receiving the polishing flux. The coil 13 is actuated by a suitable power supply (not shown), which may typically be controlled by thermocouples (not shown) located within the furnace system for maintaining the crucible at a desired temperature. Baffles 18 are used to minimize heat loss from the otherwise open upper end of the furnace system 10. The basic components of the furnace system 10 are commercially available, e.g., as the Thermco Mini-Brute furnace model MB-71, manufactured by Thermco Products Corporation, 1465 No. Batavia St., Orange, Calif., 92667.

Substrates having a very high quality surface finish, suitable for use in applications which require defect-free surfaces, may be prepared by (1) heating the flux constituents in the crucible at a sufficient temperature to melt and homogenize the constituents; (2) establishing thermal equilibrium of the molten flux at a temperature sufficient to dissolve material from the surface of the substrate at a desired rate; (3) moving a substrate at a controlled rate toward the molten flux to establish thermal equilibrium in the substrate; (4) immersing the substrate in the molten flux to dissolve a desired thickness of material from the substrate and (5) withdrawing the substrate from the flux at a controlled rate to cool the substrate without thermal shock.

According to the first step of the process, flux constituents such as lead monoxide and boric anhydride in the exemplary weight ratio of about 50:1 are mixed and melted in the crucible 17 to form a chemical polishing flux 20. The temperature proximate to the crucible is maintained above 800°C, and preferably within the approximate range 1,100°–1,200°C, to ensure adequate melting and homogenization of the constituents.

Pursuant to the second step, the crucible 17 is brought to an equilibrium temperature that is sufficient to rapidly, yet controllably, dissolve material from the surface of the substrate 11, which is typically a metallic oxide material. Where the metallic oxide substrate 11 comprises a garnet material, temperatures above approximately 860°C are preferred to achieve fast, controllable dissolution rates. Below 860°C, there is a tendency to preferentially etch the garnet substrate, e.g., at grain boundaries. While most temperatures above 860°C are satisfactory, a preferred temperature range of 885°C to 955°C has been demonstrated.

According to step three, holder 19 is used to insert the substrate 11 (or a plurality thereof) into the furnace 10 to a position just above the surface of the molten flux 20 contained in the crucible 17. In order to prevent thermal shock to the small substrate 11, the insertion must be made at a controlled rate. When polishing a garnet substrate about 1 inch in diameter and about 0.030 inches thick, the substrate may be inserted at a rate of about 5 inches per minute to a hold position about one-fourth inch above the surface of the flux melt without producing thermal shock. Thermal equilibrium is established in about 60 seconds at this hold position.

After the hold cycle pursuant to step three, the substrate is submerged in the molten salt flux according to step 4 to dissolve or strip defective material from the substrate surfaces. Again using the 1 inch diameter garnet substrate as an example, when the molten flux is maintained at a temperature of 885°C, the material is stripped from the substrate surface at the rate of about 4 microns per minute.

The dissolution rate may be increased or decreased by increasing or decreasing the temperature of the molten salt flux. In addition, a material that is compatible with the flux and the substrate material may be formed in or added to the flux mixture to modify the dissolution rate. The modifying material increases the saturation temperature of the flux and thereby decreases the dissolution rate provided by the flux. Illustratively, where the substrate material is gadolinium gallium garnet,  $Gd_3Ga_5O_{12}$ , a modifying garnet phase ( $EuEr_2$ ) ( $Ga_{0.7}Fe_{4.3}O_{12}$ ) of varying concentrations has been formed by the addition to the flux of oxides of the constituent elements  $Eu_2O_3$ ,  $Er_2O_3$ ,  $Ga_2O_3$ , and  $Fe_2O_3$ . For garnet substrate materials, perhaps the most appropriate choice for the modifying phase would be the substrate material itself. Thus, for the gadolinium gallium garnet substrate the modifying phase would be gadolinium gallium garnet.

Next, and according to step five, the stripped substrate 11 is extracted from the melt and the furnace system 10 at a controlled rate. The rate of insertion, e.g., 5 inches per minute, is usually suitable for withdrawal also.

During withdrawal of the substrate 11, a protective lead oxide coating may be deposited on the cooling substrate surface from lead oxide vapor emanating from the melt. The lead oxide provides a non-reactive coating that prevents contamination of the otherwise susceptible, stripped substrate surface. The lead oxide coating obviates the normal choice between using the substrate immediately or rigorously cleaning the surface.

The instant chemical polishing flux and polishing method are amenable to the subsequent use of film growth techniques such as chemical vapor deposition. Prior to film growth by chemical vapor deposition, the lead oxide coating is removed by, e.g., boiling the substrate in a 20 percent  $HNO_3$  solution or a 50 percent acetic acid solution. The composition and method are particularly suited to liquid phase epitaxy film growth systems. This is because the lead oxide coating is dissolved by the lead oxide and boric anhydride flux systems which can be used in liquid phase epitaxy systems, thus precluding the necessity of cleaning the substrate prior to film growth. A suitable liquid phase epitaxy flux system for garnet film growth is reported by Leven-

stein et al in Applied Physics Letters, Vol. 19, pgs. 486-488, Dec. 1971.

The lead monoxide-boric anhydride composition and the polishing method of the present invention have proven outstanding in removing sources of surface stress and imperfections that serve as pinning sites when bubble domain materials are grown on mechanically polished metallic oxide substrates. Specific applications include the polishing of gadolinium gallium garnet ( $Gd_3Ga_5O_{12}$ ) for the deposition of  $Y_3Fe_5O_{12}$ ,  $Y_3(FeGa)_5O_{12}$ ,  $(YGd)_3(FeGa)_5O_{12}$ ,  $(YGdTm)_3(FeGa)_5O_{12}$  and  $(YSm)_3(FeGa)_5O_{12}$ .

Compositions suitable for use in the present invention may also be formed by combining lead fluoride, or vanadium pentoxide, or iron oxide and lithium carbonate with lead monoxide and boric anhydride. In addition, barium oxide and/or barium fluoride may be combined with boric anhydride. Specific examples include lead monoxide, boric anhydride and vanadium pentoxide in the approximate weight ratios 50:1:2; and boric anhydride, barium oxide and barium fluoride in the approximate weight ratios 1:2:1.

A salt flux for polishing magnesia ( $MgO$ ) and spinel ( $MgAl_2O_4$ ) substrates may be formed from various weight ratios of the constituents iron oxide, lithium carbonate, lead monoxide and boric anhydride. In applying the instant polishing method, the minimum dissolution (polishing) temperatures for magnesia and spinel are approximately 800°C and 840°C, respectively.

Thus, there has been described a method of chemically polishing metallic oxide substrates. Preferred constituents, temperatures and the like have been suggested. Alternative parameters and materials have been indicated. The scope of the invention is limited, however, only by the claims appended hereto and equivalents thereto.

Having thus described a preferred embodiment of the invention, what is claimed is:

1. A method of chemically polishing metallic oxide substrates comprising the steps of:

forming a molten flux from constituents suitable for dissolving metallic oxides wherein the constituents are boric anhydride and one or more of the group consisting of lead monoxide, lead fluoride, barium oxide, barium fluoride, iron oxide, lithium carbonate and vanadium pentoxide and wherein forming the molten flux comprises mixing the constituents of the flux at a first temperature suitable for establishing a molten homogeneous solution and bringing the molten solution to thermal equilibrium at a second temperature suitable for providing a desired dissolution rate of the substrate material; moving the substrate at a controlled rate toward the molten flux to heat the substrate without thermal shock; immersing the substrate in the molten flux for a sufficient time to strip a predetermined thickness of material from the substrate; and withdrawing the substrate from the flux at a controlled rate to cool the substrate without thermal shock.

2. A method of chemically polishing a metallic oxide substrate as defined in claim 1, wherein the constituents are boric anhydride and lead monoxide.

3. A method of chemically polishing a metallic oxide substrate as defined in claim 1, wherein the constitu-

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ents are boric anhydride, iron oxide, lead monoxide and lithium carbonate.

4. A method of chemically polishing a metallic oxide substrate as defined in claim 2, wherein the step of withdrawing the substrate from the molten flux at a controlled rate causes vaporized lead monoxide to be deposited on the cooling substrate surface.

5. A method of polishing metallic oxide substrates, comprising the steps of:

mixing a molten salt flux of lead monoxide and boric anhydride in weight ratios within the range 30:1 to 50:1 at a temperature above approximately 800°C; bringing the molten salt flux to thermal equilibrium at a temperature above about 860°C;

advancing metallic oxide substrates at a controlled rate to a position proximate the molten salt flux; immersing the substrates in the molten salt flux to strip a predetermined thickness of material from the surfaces thereof; and

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withdrawing the substrates from the molten salt flux at a controlled rate to cool the substrates without thermal shock and to deposit vaporized lead monoxide on the cooling substrate surfaces.

6. A method of polishing metallic oxide substrates as defined in claim 5, wherein the flux is mixed at a temperature within the approximate range 1,100°-1,200°C.

7. A method of polishing metallic oxide substrates as defined in claim 5, wherein the molten salt flux is brought to equilibrium at a temperature within the approximate range 885°-955°C.

8. A method of polishing metallic oxide substrates as defined in claim 5, wherein the flux contains a constituent selected from  $Gd_3Ga_5O_{12}$  and  $(EuEr_2)(Ga_{0.7}Fe_{4.3})O_{12}$  for increasing the saturation temperature of the flux to decrease the substrate dissolution rate.

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